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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designation US*

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COATED SODIUM PERCARBONATE PARTICLES, PROCESS FOR THEIR PREPARATION, THEIR USE AND DETERGENT COMPOSITIONS CONTAINING THEM

(57) Abstract: Coated sodium percarbonate particles containing a sodium percarbonate core surrounded by at least one coating layer comprising at least one inorganic coating material, the coated particles having a content of available oxygen of at least 3 % by weight, and being fizzy to such an extent that 2 g of the coated particles dissolved in 50 ml of water at 20°C generate more than 0,4 ml of gas after 2 min. Process for the preparation of such coated sodium percarbonate particles comprising a heat treatment.

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COATED SODIUM PERCARBONATE PARTICLES, PROCESS FOR THEIR PREPARATION, THEIR USE AND DETERGENT COMPOSITIONS CONTAINING THEM

The present invention is related to sodium percarbonate particles with fizzing properties (also called effervescent properties).

It is known, as disclosed in the British patent GB 1494543, to treat uncoated sodium percarbonate particles by heating at a temperature of 75 to 135°C for a period of time determined by the temperature, i.e. during 2-6 h at 75°C and during 5-30 min at 135°C. The so obtained product presents an improved rate of dissolution, so that it can be used as bleaching agent for clothing for instance, and becomes effervescent. However, when incorporated into detergent compositions, where it is brought into contact with substances which enhance the decomposition of sodium percarbonate, its stability becomes too poor.

The present invention aims to overcome this drawback by providing a new product which presents fizzing properties and thus an improved rate of dissolution when used as bleaching agent in an aqueous medium, and which is sufficiently stable to be incorporated into detergent compositions which contain substances that are detrimental to its stability, such as zeolites.

The invention is therefore related to coated sodium percarbonate particles containing a sodium percarbonate core surrounded by at least one coating layer comprising at least one inorganic coating material, the coated particles having a content of available oxygen of at least 3 % by weight, and being fizzy to such an extent that 2 g of the coated particles dissolved in 50 ml of demineralised water at 20°C generate more than 0,4 ml of gas after 2 min.

"Fizzy property" intends to denote the capacity to generate gas, for instance in the form of visible bubbles, when dissolved in water, the gas escaping from the water. The gas can be mainly oxygen.

One of the essential characteristics of the invention resides in that the sodium percarbonate inside the core material, although it is surrounded by a protective coating layer, still presents fizzing properties. It has indeed been shown surprisingly that the presence of a protective stabilizing coating layer which has the function of protecting the sodium percarbonate core from the outer

atmosphere and from other surrounding detergent constituents, does not affect the fizzing properties of the sodium percarbonate inside the core.

The method used to measure fizzing according to the invention consists in dissolving 2 g, or 1 g if the product is very fizzy, of the sodium percarbonate particles in 50 ml of demineralised water at 20°C during 2 min without stirring. The amount of gas generated during these 2 min is measured by displacement of water in a connected graduated tube.

The coated sodium percarbonate particles of the invention present generally fizzing properties to such an extent that, when dissolving 2 g, or 1 g if the product is very fizzy, at least 0,5 ml of gas is generated in the method described above, in particular at least 0,6 ml, values of at least 0,7 ml being usual. Sodium percarbonate particles which generate in the above method volumes of at least 0,8 ml of gas give good results, those generating volumes of at least 0,9 ml being particularly satisfactory and those generating volumes of at least 1,0 ml of gas being especially preferred. The gas volumes generally do not exceed 10 ml, in particular not exceeding 8 ml, and in most cases not exceeding 5 ml.

The coated sodium percarbonate particles of the invention present usually a content of available oxygen of at least 5 % by weight, in particular at least 7,5 % by weight, contents of at least 10 % by weight being satisfactory and those of at least 11 % by weight being possible. The content of available oxygen is generally at most 14 % by weight, especially at most 13 % by weight. The content of available oxygen is measured by titration with potassium permanganate after dissolution in sulfuric acid (see ISO standard 1917-1982).

The inorganic coating material present in the coating layer of the coated sodium percarbonate particles of the invention can contain one or more materials selected from alkali metal and/or alkaline earth metal (particularly sodium or magnesium) salts of mineral or other inorganic acids and especially sulfate, carbonate, bicarbonate, phosphate and/or polymeric phosphates, silicates, borates and the corresponding boric acids. Particular combinations of coating agents include carbonate/sulfate, and boric acid or borate with sulfate and the combination of a) sulfate, carbonate, carbonate/sulfate, bicarbonate, boric acid, borate, boric acid/sulfate, or borate/sulfate, with b) silicate. Preferably, the inorganic coating material contains sodium silicate, sodium borate, boric acid, sodium carbonate, sodium sulfate, magnesium sulfate or one of their mixtures.

The coating layer present in the sodium percarbonate particles of the invention represents in general from 0,1 to 20 % by weight of the coated sodium percarbonate particles, in particular from 0,5 to 10 % by weight, values from 1 to 5 % by weight giving good results.

The coated sodium percarbonate particles of the invention usually have a 90 % dissolution time of at least 0,5 min, in particular at least 0,9 min. Generally, the 90 % is at most 3 min, especially at most 2,5 min. The 90 % dissolution time is the time taken for conductivity to achieve 90 % of its final value after addition of the coated sodium percarbonate particles to water at 15°C and 2 g/l concentration. The method used is adapted from ISO 3123-1976 for industrial perborates, the only differences being the stirrer height that is 1 mm from the beaker bottom and a 2 liter beaker (internal diameter 120 mm).

The coated sodium percarbonate particles of the invention have generally a mean diameter of at least 400 µm, in particular at least 500 µm. The mean diameter is usually at most 1200 µm, especially at most 900 µm.

The coated sodium percarbonate particles of the invention usually have a bulk density of at least 0,8 g/cm^3, in particular at least 0,9 g/cm^3. It is generally at most 1,2 g/cm^3, especially at most 1,1 g/cm^3. The bulk density is measured by recording the mass of a sample in a stainless steel cylinder of internal height and diameter of 86,1 mm, after running the sample out of a funnel (upper internal diameter 108 mm, lower internal diameter 40 mm, height 130 mm) placed 50 mm directly above the receiver.

The coated sodium percarbonate particles of the invention usually have an attrition measured according to the ISO standard method 5937-1980 of at most 10 %, in particular at most 8 %, especially at most 4 %. The attrition is in most cases at least 0,05 %.

The coated sodium percarbonate particles of the invention usually have a thermal stability, measured using microcalorimetry at 40°C, of at most 12 µW/g, especially at most 4 µW/g. Values of at most 3 µW/g give good results. The thermal stability is in most cases at least 0,1 µW/g. The measurement of thermal stability consists of using the heat flow or heat leakage principle using a LKB 2277 Bio Activity Monitor. The heat flow between an ampoule containing the coated sodium percarbonate particles and a temperature controlled water bath is measured and compared to a reference material with a known heat of reaction.

The coated sodium percarbonate particles of the invention present in general a moisture pick-up when measured in a test conducted in a humidity

room at 80 % relative humidity and 32°C after 24 hours, which varies from 1 to 50 g/1000 g sample. It varies in particular from 5 to 30 g/1000 g sample, and is preferably from 10 to 15 g/1000 g sample. The moisture pick-up is measured by the test described in the international application WO 97/35951 of SOLVAY INTEROX at page 7, line 25 - page 8, line 6, the content of which is incorporated herein by reference.

The coated sodium percarbonate particles of the invention can be obtained by a process comprising a first step in which the sodium percarbonate core particles are prepared, at least one subsequent coating step in which the core particles are coated with the coating material, and a heat treatment between the first step and the subsequent step, or during the subsequent step, or after the subsequent step, the heat treatment being carried out by heating the particles up to an end temperature T and maintaining the particles during a period t at this end temperature T, T (expressed in °C) and t (expressed in min) corresponding to the formula

$T \geq 0{,}000567\ t^2 - 0{,}24\ t + 114{,}490$ when T is up to 110°C, and

$T \geq -2\ t + 150$ when T is above 110°C.

The present invention therefore also concerns a process for the preparation of the above-described coated sodium percarbonate particles, comprising a first step in which sodium percarbonate core particles are prepared, at least one subsequent coating step in which the core particles are coated with the coating material, and a heat treatment between the first step and the subsequent step, or during the subsequent step, or after the subsequent step, the heat treatment being carried out by heating the particles up to an end temperature T and maintaining the particles during a period t at this end temperature T, T (expressed in °C) and t (expressed in min) corresponding to the formula

$T \geq 0{,}000567\ t^2 - 0{,}24\ t + 114{,}490$ when T is up to 110°C, and

$T \geq -2\ t + 150$ when T is above 110°C.

The first step of the process of the invention can be any known process for the preparation of sodium percarbonate core particles. It can be for instance a liquid crystallization process such as the one described in the international application WO 97/35806 of SOLVAY INTEROX, optionally followed by a conventional drying step. It can also be a fluid bed granulation process. The first step can be carried out by reacting a hydrogen peroxide solution with a sodium carbonate solution. Alternatively, it can also be a direct process by

reaction of a hydrogen peroxide solution with solid sodium carbonate and/or bicarbonate.

In the case of a liquid crystallization process followed by a drying step, or in the case of a fluid bed granulation process, the sodium percarbonate core particles obtained in the first step of the process of the invention are dry particles of sodium percarbonate containing in general less than 1,5 % by weight of water, in particular less than 1 % by weight of water, a water content of at most 0,8 % by weight being most preferred. In the case of a liquid crystallization process without drying step, the sodium percarbonate core particles obtained in the first step of the process of the invention are wet particles containing commonly more than 1 % by weight of water, the water content being generally up to 15 % by weight.

The subsequent coating step of the process of the invention can be carried out by any known coating process, such as by bringing the sodium percarbonate core particles in contact with a solution of the coating material or with a slurry of the coating material or with the coating material in powder form. Any type of mixing process or fluid bed reactor can be used for this purpose.

The heat treatment of the process of the invention is the step which seems to confer the fizzing properties to the sodium percarbonate particles. It can be carried out before (i.e. between the first step and the subsequent step), during or after the coating step. It is preferably carried out after the coating step. When it is carried out in a separate process step, it can be done in any reactor, such as in a fluid bed reactor, oven or in a circulating air oven. A fluid bed reactor in which the sodium percarbonate particles are fluidized by an upward flow of hot air is preferred.

The heat treatment of the process of the invention consists in heating up the sodium percarbonate particles up to an end temperature T and maintaining the particles during a period t at this end temperature T. T and t respond to the formula given above. T is generally from 80 to 140°C, in particular from 90 to 130°C, temperatures ranging from 100 to 120°C being particularly satisfactory. The period t is commonly ranging from 5 min to 4 h, in particular from 5 min to 1,5 h, periods ranging from 5 min to 60 min being advantageous.

The heat treatment can be carried out at any pressure. Pressures near or equal to atmospheric pressure are preferred.

The heat treatment of the process of the invention is advantageously followed by a cooling step. This can be done in a fluid bed with cooling air, by

contact with cooled plates, by cooling with air in a thin layer, or in a cooled screw conveyor. The sodium percarbonate particles are preferably cooled to a temperature below 70°C, especially below 30°C.

The sodium percarbonate particles of the invention can advantageously be used as active bleach constituent in detergent compositions.

The present invention therefore concerns also the use of the above-described sodium percarbonate particles as active bleach in detergent compositions.

The present invention also concerns detergent compositions containing the above-described sodium percarbonate particles as active bleach constituent. The detergent compositions can also contain a builder, either zeolitic or non-zeolitic. The detergent compositions can also contain other constituents such as surfactants, anti-redeposition and soil suspension agents, bleach activators, optical brightening agents, soil release agents, sud controllers, enzymes, fabric softening agents, perfumes, colours and processing aids.

The detergent compositions can take any form such as powders, tablets, liquids, etc.

Examples

Commercial coated sodium percarbonate particles of SOLVAY with an initial content of available oxygen of 13,96 % by weight have been heat treated in a fluid bed with constant air supply at different temperatures. The time and temperature of the heat treatments are given in the table below. 500 g of coated sodium percarbonate particles were used per test. The thus treated particles were then cooled down to ambient temperature. The so obtained particles were analyzed in order to measure their final content of available oxygen and their fizzyness according to the method described above by dissolving 1 g. The results are given in the table below.

Example	Time t of the heat treatment (min)	Temperature T of the heat treatment (°C)	Final content of available oxygen (% wt)	Fizzyness (ml)
1	240	90	13.69	0.5
2	150	100	13.49	1.1
3	60	110	12.99	2.0
4	45	120	12.39	3.2
5	30	130	9.75	5.8
6	15	140	9.69	6.15

CLAIMS

1 - Coated sodium percarbonate particles containing a sodium percarbonate core surrounded by at least one coating layer comprising at least one inorganic coating material, the coated particles having a content of available oxygen of at least 3 % by weight, and being fizzy to such an extent that 2 g of the coated particles dissolved in 50 ml of water at 20°C generate more than 0,4 ml of gas after 2 min.

2 - Coated sodium percarbonate particles according to claim 1, being fizzy to such an extent that 2 g of the coated particles dissolved in 50 ml of water at 20°C generate at least 1 ml of gas after 2 min.

3. – Coated sodium percarbonate particles according to claim 1 or 2, being fizzy to such an extent that 1 g of the coated particles dissolved in 50 ml of water at 20° C generate at least 0,4 ml of gas after 2 min.

4 - Coated sodium percarbonate particles according to any of claims 1 or 3, having a content of available oxygen of at least 10 % by weight.

5 - Coated sodium percarbonate particles according to any of claims 1 to 4, in which the inorganic coating material is chosen from sodium silicate, sodium borate, boric acid, sodium carbonate, sodium sulfate, magnesium sulfate and their mixtures.

6 - Process for the preparation of the coated sodium percarbonate particles of any of claims 1 to 5, comprising a first step in which the sodium percarbonate core particles are prepared, at least one subsequent coating step in which the core particles are coated with the coating material, and a heat treatment carried out between the first step and the subsequent step, or during the subsequent step, or after the subsequent step, the heat treatment being carried out by heating the particles up to an end temperature T and maintaining the particles during a period t at the end temperature T, T (expressed in °C) and t (expressed in min) corresponding to the formula

$T \geq 0{,}000567\ t^2 - 0{,}24\ t + 114{,}490$ when T is up to 110°C, and

$T \geq -2\ t + 150$ when T is above 110°C.

7 - Process according to claim 6, in which the end temperature T of the heat treatment ranges from 80 to 140°C.

8 - Process according to claim 6 or 7, in which the period t of the heat treatment ranges from 5 min to 4 h.

9 - Process according to any of claims 6 to 8, in which the heat treatment is carried out in a fluid bed reactor in which the particles are fluidized by an upward flow of hot air.

10 - Use of the coated sodium percarbonate particles of any of claims 1 to 5 as active bleach constituent in detergent compositions.

11 - Detergent compositions containing the coated sodium percarbonate particles of any of claims 1 to 5 as active bleach constituent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/14815

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B15/10 C11D17/00 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/127168 A1 (HESSBERGER WALDEMAR ET AL) 12 September 2002 (2002-09-12) paragraph '0028!; claims	1-11
Y	GB 1 494 543 A (KAO CORP) 7 December 1977 (1977-12-07) cited in the application page 1, line 68 - line 82 page 2, line 4 - line 46 page 2, line 119 - line 124 table 1	1-11
Y	EP 0 623 553 A (MITSUBISHI GAS CHEMICAL CO) 9 November 1994 (1994-11-09) claims; examples	1-11

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 April 2004	21/04/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van der Poel, W

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Form PCT/ISA/210 (second sheet) (January 2004)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 193 977 A (KIKUCHI MINORU ET AL) 18 March 1980 (1980-03-18) the whole document	1-11
X	US 3 953 350 A (NISHIMURA MASAAKI ET AL) 27 April 1976 (1976-04-27) the whole document	1-11
X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 187 (C-592), 2 May 1989 (1989-05-02) & JP 01 014103 A (TOKAI DENKA KOGYO KK), 18 January 1989 (1989-01-18) abstract	1-11
X	EP 0 884 276 A (MITSUBISHI GAS CHEMICAL CO) 16 December 1998 (1998-12-16) example 1	1-11
A	EP 0 567 140 A (KAO CORP ;NIPPON PEROXIDE CO LTD (JP)) 27 October 1993 (1993-10-27) claims; examples	1-11
A	EP 0 459 625 A (MITSUBISHI GAS CHEMICAL CO) 4 December 1991 (1991-12-04) claims; examples	1-11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 03/14815

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-11 relate to a product, the method of preparation of that product and its used, defined (inter alia) by reference to the following parameter:

P1: the coated sodium percarbonate being fizzy to such an extent that 2g of the coated particles dissolved in 50 ml of water at 20°C generate more than 0.4 ml of gas after 2 min.

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 84 EPC. It is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to:

Coated percarbonate products and methods for making them which appear to exhibit a certain effervescence (fizziness) and coated percarbonate products which are prepared according to the method of claims 6-9.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 03/14815

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